

Form Approved  
OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY)

3. DATES COVERED (From - To)

5a. CONTRACT NUMBER	
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FD-401-71-a-2-15

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER	
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5d. PROJECT NUMBER	
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DARP

5e. TASK NUMBER

A205

5f. WORK UNIT NUMBER

## 8. PERFORMING ORGANIZATION REPORT

10. SPONSOR/MONITOR'S ACRONYM(S)

Air Force Research Laboratory (AFMC)  
AFRL/PRS  
5 Pollux Drive  
Edwards AFB CA 93524-7048

11. SPONSOR/MONITOR'S  
NUMBER(S)

## 12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

### 13. SUPPLEMENTARY NOTES

## 14. ABSTRACT

20021212 128

## 15. SUBJECT TERMS

**16. SECURITY CLASSIFICATION OF:**

## 17. LIMITATION OF ABSTRACT

18. NUMBER OF PAGES

19a. NAME OF RESPONSIBLE PERSON

Leilani Richardson

a. REPORT

b. ABSTRACT

**c. THIS PAGE**

**Unclassified**

**Unclassified**

Unclassified

19b. TELEPHONE NUMBER

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Standard Form 298 (Rev. 8-98)  
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Ashwani Vij (ERC) et al., "Experimental Detection of the Pentazole Anion, N<sub>5</sub>"

**Publication in *Science* (magazine)**  
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## Experimental Detection of the Pentazole Anion, $N_5^-$

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The pentazole anion has been generated from *para*-hydroxyphenylpentazole and identified by electrospray ionization mass spectrometry. Whereas at low collision voltages the *para*-phenoxypentazole anion undergoes stepwise  $N_2$  elimination generating the corresponding azide and nitrene, at high collision voltages the  $N_5^-$  anion is formed. Fragmentation of the pentazole anion produces the  $N_3^-$  anion as the principal negative ion. These experiments provide the first experimental proof for the existence of the pentazole anion. They also demonstrate that under suitable reaction conditions the C-N bond in a phenylpentazole can selectively be broken with conservation of the pentazole ring, thus providing a potential synthetic route to the pentazole anion.

Nitrogen and oxygen are unique among the chemical elements. In contrast to the other elements, their homonuclear single bond energies are significantly less than one half of their double bond or one third of their triple bond energies. Consequently, homonuclear polynitrogen and polyoxygen species are thermodynamically highly unstable and the

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number of known compounds is very limited. Due to the highly endothermic heats of formation, their syntheses and handling present great challenges. It is therefore no surprise that for oxygen only one metastable allotrope, i. e., ozone, is known and for nitrogen none are known that can be isolated in bulk, while most other elements can exist in the form of many stable allotropes.

Polynitrogen compounds have been studied extensively for the last two decades. In view of the great experimental difficulties, most of the efforts have been limited to theoretical studies (1-9). The first major breakthrough in the synthesis area was achieved in 1999 with the synthesis of the  $N_5^+$  cation in the form of a marginally stable  $AsF_6^-$  salt (10). Subsequently, the thermally more stable  $N_5^+SbF_6^-$  was synthesized, and the crystal structure of  $N_5^+Sb_2F_{11}^-$  was determined (11).

Based on Born-Haber cycle considerations, the stability of an ionic salt is governed by four factors: the lattice energy, the electron affinity of the cation, the first ionization potential of the anion, and the activation energy barriers of the ions toward decomposition. Theoretical calculations from our and other (1,5,8,13-19) research groups predict that the unknown pentazole anion (see Figure 1) has a first ionization potential and activation energy barrier toward decomposition that might be high enough to provide a stable salt. As a result, a worldwide effort is underway to synthesize this anion. Although the existence and stability of substituted pentazole ring compounds have been demonstrated successfully more than 40 years ago by Huisgen and Ugi (20-23) and substituted pentazoles have been well characterized (24-29), all attempts to prepare either the parent  $HN_5$  molecule (30,31) or its anion,  $N_5^-$ , have so far been unsuccessful. In this paper, we wish to report the first experimental detection of this important anion.

In our pursuit of the  $N_5^-$  anion, the following strategy was employed: (i) the use of Ugi-Huisgen-type, substituted phenylpentazoles as starting materials; (ii) the transfer of maximum negative charge to the pentazole ring by the use of highly electron donating substituents on the phenyl ring in *para*-position to the pentazole substituent to increase the aromaticity and stability of the pentazole ring, while at the same time weakening the connecting C-N bond; (iii) the selective cleavage of the C-N bond while keeping the N-N bonds of the pentazole ring intact; and (iv) the use of an analytical method that is ideally suited for the generation and detection of anions. A similar approach for steps (i) – (iii) has recently been published, but attempts to cleave the C-N bond by ozonolysis were unsuccessful (32). The reasons, outlined above, prompted us to choose *para*-hydroxy (32) or *para*-dimethylamino (22) substituted phenylpentazoles as starting materials and negative ion electron spray ionization mass spectrometry (ESIMS) (33-35) as the analytical tool.

The *para*-dimethylaminophenylpentazole and *para*-hydroxyphenylpentazole were dissolved in strongly polar solvents, such as  $CH_3CN$  or a mixture of  $CH_3OH$  and  $CH_2Cl_2$ , and infused into the spectrometer with a syringe pump. Desired negative ion peaks were mass-selected and subjected to secondary negative ion mass spectroscopy (MS/MS) at variable collision voltages.

The most interesting results were obtained with *para*-hydroxyphenylpentazole in  $CH_3CN$  solution. An intense, parent – H, peak was observed at  $m/e = 162$  and mass-selected for subsequent MS/MS studies. Using a low collision voltage of –10 Volt, the  $m/e = 162$  peak ( $OC_6H_4N_5^-$ ) underwent stepwise  $N_2$ ,  $N_2$ , and CO loss, giving rise to intense peaks with  $m/e$  values of 134 ( $OC_6H_4N_3^-$ ), 106 ( $OC_6H_4N^-$ ), and 78 ( $C_5H_4N^-$ ), respectively. The loss of the first  $N_2$  molecule is due to the opening of the pentazole ring

and produces the phenoxyazide ion. The second  $N_2$  loss occurs from the azido group and generates a nitrene. The nitrene nitrogen can readily insert into the phenyl ring, and the resulting seven-membered ring can undergo a facile CO extrusion giving a pyridine anion. Secondary fragmentation of the  $m/e = 134$  peak at a collision voltage of  $-30$  Volt gave rise to intense peaks at  $m/e = 78$  ( $C_5H_4N^-$ ),  $52$  ( $C_3H_2N^-$ ), and  $50$  ( $C_3N^-$ ). The secondary fragmentation patterns of the  $m/e = 106$  and  $78$  peaks at collision voltages of  $-75$  Volt gave only a very intense  $m/e$  peak at  $50$  ( $C_3N^-$ ).

Using high collision voltages of about  $-75$  Volt for the secondary MS of the  $m/e = 162$  peak, however, gave a very different fragmentation pattern. The only peaks observed were  $m/e = 70$ ,  $52$ ,  $50$ , and  $42$  (see Figure 2). The  $m/e = 70$  peak can only be due to  $N_5^-$ , and the  $m/e = 52$  and  $50$  peaks are due to  $C_3H_2N^-$  and  $C_3N^-$ , respectively, and, as shown above, result from the fragmentation of the pyridine anion. The  $m/e = 42$  peak is due to the azide anion,  $N_3^-$ . These results clearly demonstrate that at high collision voltages the pentazole anion is formed. The fragmentation of the  $m/e = 70$  peak to  $N_3^-$  (and neutral  $N_2$  that is not observable in the negative ion spectrum) is in accord with the theoretically predicted decomposition pathway of  $N_5^-$  (8) and further supports its identification as  $N_5^-$ . The  $N_3^-$  and  $N_2$  fragments have been calculated at the CCSD(T)/aug-cc-pVTZ level of theory to be  $60$  kJ/mol lower in energy than  $N_5^-$ , with an energy barrier of  $116$  kJ/mol to the cycloreversion (8). These values indicate that bulk  $N_5^-$  salts should be manageable on a preparative scale. Furthermore, the formation of the  $N_5^-$  peak from a starting material containing a pentazole ring and the vibrational instability of open-chain  $N_5^-$  (8), establish beyond doubt that the observed  $N_5^-$  species must be the long-sought pentazole anion.

In summary, our results constitute the first experimental detection of the pentazole anion and demonstrate that in suitably substituted phenyl-pentazoles the C-N bond can be cleaved while leaving the pentazole ring intact. Since the substituted phenylpentazoles are easily accessible, this approach holds great promise for the bulk synthesis of  $N_5^-$  salts, and experiments in this direction are in progress in our laboratories. Our results on  $N_5^+$  (10,11) and  $N_5^-$ , together with the recent observations of the  $N_4$  molecule as a metastable species with a lifetime exceeding 1 microsecond (36), the observation of a new but ill-characterized poly-nitrogen species from a discharge generated nitrogen plasma (37), and exciting progress in high nitrogen compounds (29,38), indicate a bright future for experimental polynitrogen chemistry.

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39. This work was financially supported by the Defense Advanced Research Project Agency, the Air Force Office of Scientific Research, and the National Science Foundation. The authors are grateful to Drs. Robert Corley, Arthur Morrish, Don

Woodbury, and Michael Berman for their steady support, to Prof. W. Kaska for the use of the ESIMS, and to Drs. Michael Gerken, Thorsten Schroer, Stefan Schneider, Ralf Haiges, and Ross Wagner for support and stimulating discussions.

#### FIGURE CAPTIONS

1. Minimum energy structure of the planar  $D_{5h}$  pentazole anion from ref.1, calculated at the CCSD(T)/aug-cc-pVTZ level of theory, bond length in Å.

2. Negative ion mass spectrum of the mass-selected  $m/e = 162$  peak due to  $\text{OC}_6\text{H}_4\text{N}_5^-$ , recorded at a collision voltage of  $-75$  Volt. The peaks at  $m/e = 70$  and  $42$  are due to the  $\text{N}_5^-$  anion and its decomposition product  $\text{N}_3^-$ , respectively, while the peaks at  $52$  and  $50$  are the  $\text{C}_3\text{H}_2\text{N}^-$  and  $\text{C}_3\text{N}^-$  fragments, respectively, resulting from the breakdown of the phenoxyazide anion.



